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(54) Improved glyphosate formulations

Glyphosatformulierungen

Formulations de glyphosate

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(73) Proprietor: **MONSANTO COMPANY**
St. Louis Missouri 63167 (US)

(72) Inventors:

- Kuchikata, Masuo
Ryugasaki-City Ibaraki-Pref. (JP)
- Prill, Erhard John
Kirkwood Missouri 63122 (US)
- Richardson, Ronald Owen
Ellisville Missouri 63011 (US)
- Sato, Tatsuo
Chofu-City Tokyo (JP)
- Surgant, John Melvin
Clayton Missouri 63124 (US)
- Wright, Daniel Richard
St. Louis Missouri 63109 (US)

(74) Representative: **Bosch, Henry et al**
Monsanto Services International S.A.
Patent Department
Avenue de Tervuren 270/272
Letter Box No. 21
1150 Brussels (BE)

(56) References cited:

EP-A- 0 206 537 **EP-A- 0 255 760**
EP-A- 0 290 416 **WO-A-87/04595**
US-A- 3 799 758

- **CHEMICAL PATENTS INDEX, BASIC**
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Description

Field of the Invention

This invention relates to dry, water soluble, agriculturally acceptable herbicidal compositions useful for killing and/or controlling weeds and to a process for preparing such compositions. This invention also relates to dry, water soluble or water dispersible, granular, agriculturally acceptable herbicidal compositions containing two or more herbicides, herbicidal methods of use thereof and to a process for preparing such compositions.

Description of the Prior Art

Glyphosate (N-phosphonomethylglycine) is well known in the art as an effective herbicide. It is also known that glyphosate, an organic acid, is relatively insoluble in water. Glyphosate is typically formulated as a water-soluble salt, especially as the isopropylamine salt (IPA salt) to kill or control weeds or plants. Glyphosate is typically sold commercially as an aqueous concentrate.

Various salts of glyphosate, methods for preparing salts of glyphosate, formulations of glyphosate and methods of use for killing and controlling weeds and plants are disclosed in U.S. Patents 3,799,758 and 4,405,531 issued to John E. Franz on March 26, 1974 and September 20, 1983 respectively. Other US patents which disclose salts of glyphosate include US 4,315,765 issued to George B. Large on February 16, 1982, US 4,507,250 issued to Izak Bakel on March 26, 1985, US 4,397,676 issued to Izhak Bakel on August 9, 1983, US Patent 4,481,026 issued to Michael P. Prisbylla on November 6, 1984 and, US 4,140,513 issued to Erhard J. Prill on February 20, 1979. The aforementioned patents are incorporated herein in their entirety by reference.

EPO published patent application 204146 discloses a herbicidal composition comprising (a) 2-(4-chloror-2-fluor 5-propargyloxyphenyl)-5,6,7,8-tetrahydro-1H-1,2,4-triazolo (1,2-s)phridazine -1,3, -2H-dione (I), with (b) glyphosate (i) glufosinate (ii) bialaphos (iii) and/or paraquat (iv) or their salts and an inert carrier or diluent.

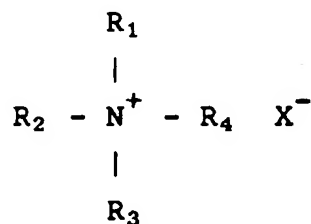
EPO published patent application 255760 discloses a granule shaped agricultural composition prepared by introducing to the top of a drying tower, a mixture of the agricultural chemical, an anionic surfactant and optionally one or more additives in the form of a concentrated solution or an aqueous slurry.

Published Japanese patent applications J62175407 and J62175408 disclose a herbicide containing solid carrier, additives and herbicidal component and has a particle size of 48-150 mesh. Disclosed herbicidal components are ((3-amino-3-carboxy)propyl-1)methylphosphonic acid, N-(phosphonomethyl)glycine, (2-amino-4-methylphosphino-butylal) alanylalanine and their salts.

Published European Patent Application 0 206 537 discloses a solid, substantially non-hygroscopic, phytoactive composition comprising an intimate mixture of a phytoactive N-phosphonomethyl-N-carboxymethyl compound and a surfactant which is solid at ambient temperatures.

Published European Patent Application 0 256 608 discloses a method for the preparation of a solid, phytoactive composition comprising (a) reacting an acid form of a phytoactive N-phosphonomethyl-N-carboxymethyl compound with a liquid amine to form the amine salt of said N-phosphonomethyl-N-carboxymethyl compound (b) admixing said amine salt of said N-phosphonomethyl-N-carboxymethyl compound with a molten surfactant, the surfactant being solid at ambient temperature and (c) cooling said mixture to a temperature below the melting point of the surfactant to form a composition comprising said surfactant and said amine salt of N-phosphonomethyl-N-carboxymethyl compound interdispersed in the matrix thereof and which is solid at ambient temperatures.

EPO Publication No. WO 87/04595 discloses a herbicidal water-soluble dry particulate glyphosate formulation comprising the sodium salt of glyphosate and a surface active agent of the formula:



wherein R_1 and R_2 are independently methyl or ethyl, R_3 is methyl, ethyl benzyl or C_{10} to C_{18} alkyl, R_4 is C_{10} to C_{18} alkyl and X is chloro or bromo.

Japanese LOP 145 205-88 discloses an aqueous concentrate herbicidal formulation comprising a water soluble glyphosate salt, ammonium sulfate and a quaternary ammonium salt.

PCT/WO 87-04,712 discloses a method of preparing a particulate alkali metal salt of N-phosphonomethylglycine which comprises adding a solid alkali metal base with agitation to N-phosphonomethylglycine containing up to 25% water.

Research Disclosure Publication 27161 November 1986 "Novel Glyphosate acid wettable powder formulation effective in control of weeds" discloses a formulation comprising N-phosphonomethylglycine, nonionic surfactant, diatomaceous earth, inorganic salt (ammonium sulphate) and an antifoaming agent.

Chemical Abstracts 103: 191395K (1985) Davydov, A.M.; Vechtomova, T.N.; Banzunova, G.G. (USSR). Sashch. Rast. (Moscow) 1985, (9), 40-1 (Russ) discloses that the 36% aq. soln. Utal (I) [96638-41-4] and the 50% wettable powder Fosulen (II) are Soviet brands of glyphosate.

Chemical Patents Index, Basic Abstracts Journal, week 8736, Section C, November 4, 1987, Abstract N° 87-253854/36 discloses solid herbicidal compositions comprising 0,5 - 3,5 wt % glyphosate or a salt thereof, 0,5 - 13 wt % aids and 79-99 wt % solid carrier. Aids are defined as oil-absorbing materials, binders and surfactants selected from polyoxyethylene alkyl ether, polyoxyethylene alkyl phenyl ether and others.

Summary of the Invention

The invention comprises a dry, water soluble, agriculturally acceptable herbicidal composition comprising N-phosphonomethylglycine or a water soluble salt of N-phosphonomethylglycine as a water soluble granule, or water soluble powder although water soluble granules are preferred. The composition comprises N-phosphonomethylglycine or a water soluble salt of N-phosphonomethylglycine, at least one surfactant which is liquid at ambient temperature and which gels in water, and less than about 5% by weight of water. In another embodiment, the invention further comprises said composition containing water.

Compositions of this invention may further comprise ammonium sulfate, potassium sulfate, potassium chloride, sodium sulfate, urea, mixtures thereof and the like. The composition may optionally include a synergist, quick-burn additive, a humectant, a co-herbicide, a dye, pigment, corrosion inhibitor, thickener, dispersing agent, calcium sequestrant, defoamer, mixtures thereof and the like. When employing two or more herbicides in the composition, the composition of this invention may be a water soluble granule.

In a process for preparing the composition of this invention, the dry, water soluble, granular, agriculturally acceptable composition is prepared by pan, extrusion, fluid bed (or equivalent) granulation of N-phosphonomethylglycine, N-phosphonomethylglycine and surfactant, or a water soluble salt of N-phosphonomethylglycine, optionally with a surfactant.

In another embodiment of this invention, said composition is prepared by admixing N-phosphonomethylglycine or an agriculturally acceptable salt of N-phosphonomethylglycine with one or more liquid surfactants.

In another method of preparing the compositions of this invention, one may admix ingredients with water and thereafter spray dry to give a granular product.

In another method of preparing the compositions of this invention, one may admix the ingredients with water and drum dry on a flaking roll and grind the flaked composition to give a granular composition.

Yet another method of preparing the granular compositions of this invention involves admixing glyphosate and base, for example ammonium bicarbonate, with water, crystallizing, centrifuging and blending in the surfactant and drying the granular product.

In still another method for preparing the granular composition of the invention, involves carrying out the reaction of the ingredients in a fluid bed drier using glyphosate wet cake or moistened glyphosate containing a minimum of moisture to provide occurrence of the neutralization phase of the process and then completion by drying to give the granular product.

Compositions may be optionally mixed with ammonium sulfate and optionally one or more additional herbicides and thereafter these ingredients blended to form said admixed composition. The order of addition of the ingredients to the starting material, typically glyphosate or a water soluble salt thereof is not critical. The admixed composition is optionally granulated with equivalent means or in an equivalent manner to form a composition of this invention.

Objects of the Invention

It is an object of this invention to provide a dry, water soluble, agriculturally acceptable herbicidal composition.

It is an object of this invention to provide a process for preparing said composition.

It is yet another object of this invention to provide a herbicidal method of use for killing and controlling weeds by applying a herbicidally effective amount of said composition to the locus of the plant or weed to be killed or controlled.

It is a further object of this invention to provide a dry, water soluble agriculturally acceptable herbicidal composition which has relatively low shipping costs, mix compatibility with various water-soluble co-herbicides, mix compatibility with

various additives which can be packaged in low cost, combustible containers and is easy to use with minimum user contact with the formulation.

These and other objects such as a uniform particle size distribution and noncaking features are achieved in this invention hereinafter described in more detail.

Another advantage offered in this invention is where a dry product would be of interest in areas of use where worker exposure is an issue. Dry formulations are excellent candidates for packaging in water-soluble bags that would substantially reduce worker exposure from handling and mixing.

Detailed Description of the Invention

The invention comprises a dry, water soluble, agriculturally acceptable herbicidal composition comprising N-phosphonomethylglycine or a water soluble salt of N-phosphonomethylglycine and a liquid surfactant which gels in water.

As employed herein, the term "liquid" comprises a substance in a flowable state at room temperature (about 25° Centigrade).

Said composition of this invention is typically greater than about 60 mesh and contains in the range from about 0.1% to about 5.0% weight and preferably less than about 2% weight percent water, although greater or lesser amounts of water (moisture) may be present depending on the composition ingredients.

If desired a co-herbicide, a corrosion inhibitor, a thickener, a dispersing agent, a calcium sequestrant, a synergist, a quick burn down additive, a humectant, a dye or pigment, defoamer may be admixed individually or collectively in the composition.

The thickener may be selected from the group consisting of sodium ligninsulfate, starches, cellulose derivatives, high molecular weight polyoxyethylenes, gums, mixtures thereof and the like.

Certain co-herbicides which form water soluble salts may be used. Such co-herbicides may be selected from the group consisting of acifluorfen (5-(2-chloro-4-(trifluoromethyl)phenoxy-2-nitrobenzoate), chloramben (3-amino-2,5-dichlorobenzoic acid), 2,4-D (2, 4-dichlorophenoxy)acetic acid), endotal (7-oxabicyclo(2.2.1)heptane-2,3-dicarboxylic acid), mecoprop ([2-(2-methyl-4-chlorophenoxy) propionic acid], picloram (4-amino-3,5,6-trichloropyridine-2-carboxylic acid), 2,4,5-T (2,4,5-trichloroacetic acid), benzac (2,3,6-trichlorobenzoic acid), dicamba (3,6-dichloro-o-anisic acid), MCPA (4-chloro-o-tolyloxyacetic acid), dalapon (2,2-dichloro-propionic acid), dichlorprop (2,4-dichlorophenoxypropionic acid), MCPB (4-(4-chloro-o-tolyloxy)-butyric acid, bialaphos (DL-homoalanin-4-yl-methylphosphinate), glufosinate (Ammonium (3-amino-3-carboxypropyl)-methylphosphinate, Pursuit (2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-5-ethyl-3-pyridine carboxylic acid), Scepter (2-[4,5-Dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-3-quinolinecarboxylic acid), mixtures thereof and the like.

The glyphosate salt component of the compositions of this invention may be preferably prepared by admixing various bases (acid acceptors) including those selected from those listed below with glyphosate wet cake or moistened glyphosate. Ammonia, ammonium hydroxide, ammonium and alkali metal carbonates, bicarbonates, meta borates, citrates, formates, oxalates, phosphates, propionates, pyrophosphates, metasilicates, orthosilicates, sulfites, thiosulfates, tetraborate, monoacid phosphates, triphosphates, metaphosphates, sodium hydroxide, potassium hydroxide, tetrasodium EDTA, mixtures thereof and the like. Mixtures of glyphosate and salts thereof may be employed as starting materials.

As employed herein, the term "admixed" includes reaction, neutralization and partial neutralization of glyphosate as well as mixed with and sprayed on, combined with or added to another ingredient(s).

Suitable gelling liquid surfactants include nonionic surfactants, anionic surfactants, cationic surfactants and amphoteric surfactants, mixtures thereof and the like, preferably ones that provide increased herbicidal activity of N-phosphonomethylglycine. Most preferred surfactant is an ethoxylated tallow amine containing 15-18 moles of ethylene oxide.

Examples of gelling liquid nonionic surfactants are polyoxyethylene alkyether, polyoxyethylene alkylarylether, polyoxyalkylene alkyl arylether formaldehyde condensates, polyoxyethylenealkylene arylether, polyoxyalkylene alkylester, polyoxyalkylene alkyl sorbitan ester, polyoxyalkylene alkyl sorbitol ester, polyoxyalkylene alkyl glycerol ester, polyoxyalkylene block copolymer, polyoxyalkylene blockcopolymer alkyl glycerol ester, polyoxyalkylene alkyl sulfonamides, polyoxyalkylene rosin ester, polyoxypropylene block copolymers, polyoxyethylene oleyl ether, polyoxyalkylene alkylphenols, mixtures thereof and the like.

Examples of gelling liquid cationic surfactants are polyoxyalkylene alkylamines such as ethoxylated tallow amine, ethoxylated oleylamine, ethoxylated soyamine, ethoxylated cocoamine, ethoxylated synthetic alkyl amines, ethoxylated III^o octyl amine, etc. and mixtures thereof.

Examples of suitable amphoteric surfactants are lauryldimethylamine oxide, Aromox C/12, amine oxides, Monaterics, Miranols, betaines, Lonzaines, other amine oxides, mixtures thereof and the like.

Preferable agriculturally acceptable salts of N-phosphonomethylglycine (glyphosate) include the ammonium, isopropylamine, trimethylsulfonium, imminourea salts, sodium, potassium, mixtures thereof and the like. The sodium and ammonium salts of N-phosphonomethylglycine are especially preferred in this invention. Mixtures of water soluble salts of N-phosphonomethylglycine may be employed herein as well as surfactant salts of N-phosphonomethylglycine including, for example, a N,N,bishydroxyethylcocoamine salt of N-phosphonomethylglycine,

Most preferred water-soluble granules (WSGs) are those made with the ammonium salt or sodium salt of glyphosate and an ethoxylated tallowamine surfactant (tallowamine + 15-20 moles of ethylene oxide) as the surfactant.

In another embodiment the composition of this invention further comprises ammonium sulfate, potassium sulfate, potassium chloride, sodium sulfate, urea, mixtures thereof and the like.

5 If desired, a dry, water soluble, agriculturally acceptable composition comprising a water soluble, agriculturally acceptable salt of N-phosphonomethylglycine may be prepared by pan granulation or extrusion granulation of the salt of glyphosate itself. If pan granulation is to be employed, an intermediate drying step after preparing the salt may be necessary before pan granulation is carried out.

10 The salt of N-phosphonomethylglycine may be prepared by admixing an acid acceptor with glyphosate acid (containing in the range from about 10 to about 15 wt % water) to neutralize the N-phosphonomethylglycine. A slight excess of acid acceptor may be preferred, however it is not required when ammonia, ammonium, hydroxide or ammonium bicarbonate is the base.

15 When the composition of this invention comprises a water soluble salt of glyphosate, the process of preparation comprises preparing said water soluble salt of glyphosate followed by granulation (pan, extrusion, fluidized bed, or equivalent such as spray drying, drum drying, flaking, crystallizing and centrifuging) to form a composition of this invention. In this embodiment, water is added in a pan granulation step to promote granulation and is thereafter removed in subsequent drying. If extrusion granulation is employed then a water removal step is usually but not always necessary.

20 A fluidized bed drying step is usually carried out following granulation to form a composition of this invention. Reworking of the granules may be necessary at times to take into account various parameters such as temperature, ingredient quality, and the like.

The process of preparation comprises admixing said water soluble, agriculturally acceptable salt of N-phosphonomethylglycine and said one or more liquid surfactants optionally with ammonium sulfate and thereafter blending these ingredients singularly or collectively to form an admixed composition as a composition of this invention.

25 The surfactant (s) may be admixed with the water soluble salt of glyphosate by spraying the surfactant on the water soluble salt of glyphosate while the water soluble salt of glyphosate is being pan granulated to form a composition of this invention. The one or more liquid surfactants may be admixed with the water soluble glyphosate salt as in a blender prior to granulation. In the latter embodiment, water is typically added to the granulator to promote granulation in forming a composition of this invention.

30 If desired in another embodiment, water may be sprayed onto the admixed composition comprising water soluble salt of glyphosate and optionally surfactant while said admixed composition is being pan granulated to form a composition of this invention.

Typically the admixed composition will have an appearance (depending on the amount of water present at that time) which ranges from a damp or moist powder, even fluffy, to that of a dough like substance after the admixing is completed in a kneader, blender or other mixer type device. Thereafter additional water present in the mixed composition may be 35 removed to a satisfactory level for granulation (pan, extrusion, fluid bed or equivalent) which may in turn be followed by fluidized bed drying. Carbon dioxide and water are removed in the drying process.

If extrusion granulation is desired, an admixed composition may be fed to an extruder without an intermediate drying and thereafter the extrusion product, the extruded admixed composition, may be further dried in a fluidized bed dryer or other drying equipment (drying oven, flash dryer, etc.) to form a composition of this invention.

40 This invention also includes a method of killing or controlling weeds by applying a herbicidally effective amount of the composition of this invention to the locus of the plant or weed to be killed or controlled. Dilution with water before application to the locus of the plant or weed is desirable although perhaps not necessary in all cases as for example when the plants contain a dew. In general when killing or controlling weeds or plants using this invention, the general methods of use disclosed in U.S. Patent 3,799, 458 for salts and compositions employing glyphosate and the other 45 patents referred to hereinabove will be useful to those of skill in the art.

The application of an effective amount of the compounds of this invention to the plant is essential for the practice of the present invention. The exact amount of glyphosate salt containing glyphosate as the active ingredient to be employed is dependent upon the response desired in the plant as well as such other factors as the plant species and stage of development thereof, and the amount of rainfall as well as the specific salt employed. In foliar treatment for the 50 control of vegetative growth, the active ingredients are applied in amounts from about 0.01 to about 20 or more pounds per acre. In applications for the control of aquatic plants, the active ingredients are applied in amounts of from about 0.01 parts per million to about 1000 parts per million, based on the aquatic medium. An effective amount for phytotoxic or herbicidal control is that amount necessary for overall or selective control, i.e. a phytotoxic or herbicidal amount. It is believed that one skilled in the art can readily determine from the teachings of this specification, and patents referred 55 herein the approximate application rate. Granules may also be applied using conventional broadcast granule techniques.

The following examples are presented to illustrate the present invention as well as some of the various embodiments of the invention. These examples are presented as being illustrative of the novel formulations, process for preparing the invention and herbicidal use thereof and are not intended to be a limitation of the scope of this invention.

EXAMPLES

GENERAL ADMIXING PROCESS:

In a typical process for preparing ammonium glyphosate water soluble granules (and optionally sodium glyphosate) water soluble granules of this invention, the process begins by neutralizing glyphosate acid wet cake (contains about 1 to about 15 % water) with ammonium bicarbonate (or sodium carbonate or sodium bicarbonate) an admixing process in a mixer such as a ribbon blender or a Hobart type mixer to form a water soluble salt of glyphosate (ammonium or sodium salt of glyphosate).

The products of the reaction include ammonium (sodium) glyphosate, carbon dioxide and water. As the reaction proceeds there is a loss in weight of the formulation. If desired, the reaction can be monitored by the rate of carbon dioxide formation and consequential weight loss. The time involved for the reaction to proceed to completion is from about twenty to thirty minutes to about one hour. The optimum particle size is about 20 mesh for the admixed composition.

After the glyphosate ammonium (sodium) bicarbonate reaction has been completed, a fluffy wet cake or white powder of ammonium (sodium) glyphosate has formed. At the time, the ammonium (sodium) glyphosate can either be subsequently formulated into a water soluble granule to form a composition of this invention or dried, or used as is for some other use such as in package mixes to also form a composition of this invention.

Surfactant Addition and Mixing

After making the ammonium (sodium) glyphosate as described above, one adds at least one surfactant. The preferred surfactant is an ethoxylated fatty tallow amine with an average ethylene oxide content of about 15-18 moles MON 0818. The addition of surfactant typically produces a very stiff dough. The mixing equipment is appropriately selected so as not only be capable of mixing a thick, stiff dough, but it must also be steam jacketed to allow heating to drive off excess water to form a damp powder in the event pan granulation is to follow as a further processing step.

Pan Granulation

If desired, the moist but free flowing ammonium (sodium) glyphosate surfactant mixture is fed into a typical pan granulator and granulated to form a composition of this invention. Water is usually added in the granulation step. In order to achieve the desired granule characteristics it may be desirable to experiment with the granulator's operating characteristics.

Another approach is to granulate the ammonium glyphosate in a piece of equipment known as a turbulator which is basically a modified pug mixer that mixes thoroughly. The powder is added at one end. Liquid is sprayed on during mixing which forms granules that come out the other end and are ready for drying. This approach could be used in place of the surfactant addition and mixing step to combine the mixing step with the granulating step. Other suitable methods of granulating could be fluid bed granulation, tumble granulation techniques, or granulating using Schugi granulation equipment.

II. METHODS OF GRANULATION

A number of different methods were used to make WSGs. Some WSGs were made by spraying a liquid surfactant directly on ammonium glyphosate powder in a pan granulator (or disk pelletizer). It was found that the surfactants could be mixed with the glyphosate powder in a blender and this mixture granulated by spraying water onto the powder. There was little difference in the granule quality. Other equipment used in the making of granules included: Patterson-Kelley V-blenders, Extruders, Ribbon Blenders, and Fluid Beds.

Extrusion Granulation

If desired, one may proceed from the first step to extrusion granulation. In that embodiment, the admixed product from the admixing device is fed to an extruder and the extruded product of this invention is typically a cyclindrical shaped particle, typically having a diameter in the range from about 0.4 to about 2.0 mm and preferably in the range from about 0.7 to 1.2 mm and having a length in the range from about 1 to 10 mm and preferably from about 2 mm. to about 5 mm.

After granulation, further drying of the composition is typically desired to form a composition of this invention.

Drying

A preferable method of drying is the use of a fluid bed drier which allows drying to occur quickly and more temperate than other methods. For small size samples, drying can be accomplished in a 60°C to 70°C in a few hours or in an oven overnight.

The water content of the sodium glyphosate powder was also found to have an effect on the size granules formed in a pan granulator and on the quality of the WSG. Sodium glyphosate powder can be a free flowing powder while containing as much as about 18-20% water. It was found that a minimum water content of about 5-7% was needed to form granules of good quality. About 10 to 15% were found to be the optimum water content. When the water content was below about 5-7% for pan granulation the sodium and ammonium glyphosate granules that would form would be extremely soft and powdery on the inside.

Water could be employed in the glyphosate powder to be granulated or, if desired, the surfactant can be mixed with water that is sprayed on the powder. An optimum water content for granulation was one in which the total amount of water amounted to approximately 10% of the glyphosate weight.

A minimum water content was found to be necessary even when the process to make the granules was changed such that the surfactant was blended in a mixer with the ammonium glyphosate powder and the resultant powder granulated. When "bone dry" ammonium glyphosate was mixed with Sterox NJ (nonyl phenol + 9.5 moles EO) and the resulting powder granulated, the granules were soft. If the ammonium glyphosate contained about 10% water when the surfactant was mixed in, the granules formed were of very good quality.

The water seems to be necessary only while the granules are forming. Once the granules are formed, the water can be removed by drying and the granules will be high quality, sturdy granules.

The water can be removed either in an oven or fluid bed drier.

Without being bound by theory, the relationship between water, surfactant ethylene-oxide (EO) content and granule quality seems to suggest a hydrogen bonding or hydration between the surfactant and glyphosate. Surfactants that do not gel in water, in general, do not yield granules of good quality.

The following examples were prepared in general accordance with the above general procedures although departures were employed to adjust for batch size and general equipment availability. The identity and quantity of ingredients are provided for each composition. All percents (%) are on a weight basis.

EXAMPLE 1

Ammonium bicarbonate was admixed with glyphosate acid and the mixture was thereafter dried

Glyphosate acid (100%)	90.86 grams
Ammonium bicarbonate	43.52
Water and carbon dioxide lost	- 34.38 grams
	100.00 grams

EXAMPLE 2

Glyphosate Acid wet cake (86%)	105.65 grams
Ammonium bicarbonate	43.52 grams
	149.17 grams

The above ingredients were weighed together and mixed in a beaker with a spatula to form ammonium glyphosate. The temperature of mixture dropped.

The final temperature was 7°C. Weight steadily decreased.

Final loss while mixing after about 2 hours on a Roller Mill was 21.76 grams.

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The ammonium glyphosate was dried in an 60°C oven overnight.

Loss	22.41 grams.
Total weight	105.00 grams

EXAMPLE 3

To the ammonium glyphosate (prepared in Example 2 above) was added Genamin T-150 (tallow amine plus 15 moles ethylene oxide (E.O.) was used. A dry solid was formed.

Ammonium glyphosate	65% wt.
Genamine T-150	23%
Ammonium Xylene Sulfonate	20
Water and inerts	10

The formulation was prepared by first adding Genamin T-150 to wet cake glyphosate and mixing by hand. Ammonium bicarbonate was added. Reaction seemed much slower and incomplete.

The combining of T-150 (tallow amine + 15 mole E.O.) with water in the glyphosate wet cake appeared to make water less available for dissolving ammonium bicarbonate and reacting with the wet cake.

Ammonium xylene sulfonate 40 (AXS-40) was added and mixed into the formulation to thin out the gel structure. Weight loss increased at a similar rate as without T-150. The amount of AXS-40 in the final formulation was 7%. The mixture was dried in 60° oven.

EXAMPLE 4

Ammonium glyphosate was made by adding ammonium bicarbonate to wet cake (see Example 2).

This time the formulation was dried before adding Genamin T-150. Again, theoretical weight loss agreed well with actual weight loss.

Genamin T-150 was added at 25% level of the formulation and mixed in. The formulation was not dry and free flowing. The sample was placed in 60°C oven overnight. The sample was still gooey.

Another sample was prepared. Again, similar results were obtained. 25% water (in regard to formulation) was sprayed on and mixed in. The formulation heated up, not significantly, but noticeably. The sample was placed in 60°C oven overnight. Dry chunks of free flowing solid were formed.

EXAMPLE 5

Formulation:	
Ammonium Glyphosate	64.64%
Ethomeen T-25*	25.30%
TH Antifoam 30 Ind**	1.02%
Water & Inerts	8.86%
	<u>100.00%</u>

* Tallowamine + 15EO

** Silicone defoamer

This composition was prepared by hand with a beaker and a spatula. Assayed at 60.64% glyphosate.

EXAMPLE 6

Formulation:	
Ammonium Glyphosate	56.95%
Ethomeen T-25	28.05%
Sodium Lauryl Sulfate	5.00%
TH Antifoam 30 Ind	1.02%
Water & Inerts	8.08%
	100.00%

This composition was prepared by a beaker and a spatula.

EXAMPLE 7

Ammonium glyphosate (91% acid equivalent)	800 grams
Water	50 grams
Ethomeen C-15	150 grams
Initial pan and extrusion granulation looked good.	

EXAMPLE 8

Ammonium glyphosate	250 grams
Sorbitol (solid)humectant	250 grams
Ethomeen T-25 liquid surfactant	80 grams

EXAMPLE 9

This formulation was made by adding solids in a jar and then mixing on roller mill.

Glyphosate acid wet (86%)	250 grams
Ammonium bicarbonate	90 grams
Ammonium sulfate (granular)	600 grams
Mixed these for 1 hour.	
Sprayed on Ethomeen T-25	67 grams
Dried after T-25 was added.	

The above composition was made in a Patterson Kelley Blender.

EXAMPLE 10

Ammonium glyphosate was prepared from glyphosate using the ammonia bicarbonate method in a ribbon mixer. Three hundred pounds of glyphosate wet cake acid was dried by placing it in 2 inch high trays and leaving it open to the air. The dry glyphosate acid was then Fitz milled to uniform size. Initial moisture was about 16%, after 2 days in the open the moisture content was 1.25%.

Glyphosate acid	150 pounds
Ammonium bicarbonate	70 pounds
Water	4 pounds
Flo Mo TA-15 *	17 pounds

* Tallowamine + 15 E.O.

The ammonium bicarbonate was added as by hand as lumps to glyphosate acid in the ribbon mixer. Water was added to speed up the reaction. The reaction took 2.5 hours. Some ammonia bicarbonate lumps were left which needed to be broken up for better reaction rates. The final mixture was Fitz-milled to breakup the lumps. Additional granulation was not needed.

EXAMPLE 11

Using the same ribbon mixer as in Example 10, a step up was attempted. For the first trial dry glyphosate acid was used.

Ammonium sulfate	150 pounds
Glyphosate acid (97%)	51.5pounds
Ammonium bicarbonate	12.0pounds
Water	4.0pounds

These four ingredients were mixed together and then FLOMO TA-15 (17.0 pounds) was added to make a total of 234.5 pounds. This produced good mixing and allowed lumps to be broken up. Good granules formed upon drying.

EXAMPLE 12

Ammonium sulfate	11125 grams
Glyphosate acid	2500 grams
Ammonium bicarbonate	560 grams
Ethomeen T-25	1042 grams
Water and carbon dioxide loss	-663 grams

The formulation was made in Patterson Kelley blender with the water content at 2.94%. Granulates were fine in size.

EXAMPLE 13

Ammonium glyphosate (86.5%)	83.24%
Ethomeen T-25	16.76%

Made 7000 grams in Patterson Kelley blender

EXAMPLE 14

	%
Glyphosate wet cake (86%)	22.0
Diammonium phosphate	14.0
Sorpol 7553	6.0
Ammonium sulfate	58.0
	<u>100.00</u>

EXAMPLE 15

	%
Glyphosate wet cake (91.0%)	22.4
Sodium bicarbonate	9.5
Sorpol 7553	6.0
Ammonium sulfate	73.0
	<u>100.00</u>

EXAMPLE 16

	%
Glyphosate wet cake (85%)	22.4
Sodium hydroxide	4.5
Sorpol 7553	6.0
Ammonium sulfate	73.0
Water lost or drying	-5.9
	<u>100.00</u>

EXAMPLE 17

	%
Glyphosate wet cake (82.2%)	20.42
Dicamba (88.8%)	9.34
Sodium bicarbonate	18.95
Sorpol 7553 *	4.15
Monoammonium phosphate	47.14
	<u>100.00</u>

* Tallowamine + 15EO

EXAMPLE 18

	%
Glyphosate wet cake (81.2%)	28.38
Sodium bicarbonate	11.48
Ammonium sulfate	5.18
Sorpol 7553	54.96
	<u>100.00</u>

EXAMPLE 19

	%
Ammonium glyphosate *	72.09
Sterox NJ **	27.01
	<u>100.00</u>

* Prepared from glyphosate wet cake and ammonium bicarbonate

** Nonyl phenol + 9.5 EO

EXAMPLE 20

	%
Sodium glyphosate	16.07
Sorpol 7553	3.04
Ammonium sulfate	46.06
Bialaphos WSG (20% a.e.) *	37.03
	<u>100.00</u>

* Herbiace WSG

EXAMPLE 21

	%
Ammonium glyphosate	73
Surfactant *	22
Water	5
	<u>100</u>

* 3:1 blend of Sterox NK (nonyl phenol + 11 E.O.): Aromox C-12 (N,N-bis(hydroxyethyl)cocoamine oxide)

EXAMPLE 22

	%
Ammonium glyphosate	1000 lbs.
T-DET N-307 *	500 lbs.
Water loss on drying	-173 lbs.

* Nonylphenol + 30 moles E.O.

A spray dry process for preparation of the granular product of this invention involves use of a feed stock consisting of an aqueous solution or slurry or combination thereof of the ingredients (glyphosate salt, or glyphosate and base, surfactant and additives such as ammonium sulfate, a solid water-soluble co-herbicide, if desired) with a total solids content of 45-65%.

The spray tower size may vary greatly from a pilot unit of 6' diameter x 15' height to a commercial unit of 22' diameter x 30' vertical height or larger equipped with a 30° - 60° collection cone, if desired.

Temperature of slurry: 20-50°C

Spray mode: Mixed flow or co-current Laminar.

Atomization Nozzle: Hollow cone (1-3 nozzles)

Spray Pressures: 60-250 psi

Air Flow: 625-4200 CFM

Tower Air Temperature: Inlet: 250-400°F

Outlet: 100-300°F

Ingredients may be admixed in the order listed until uniform in a plastic bag. The admixed composition may be granulated using pan granulator. Water can be sprayed on during granulating and a standard pan granulation procedure used. The granules may be dried in a lab fluidized bed.

Claims

1. A dry water-soluble agriculturally acceptable composition comprising N-phosphonomethylglycine or a water soluble salt of N-phosphonomethylglycine, at least one surfactant which is liquid at ambient temperature and which gels in water, and less than about 5% by weight, preferably less than about 2% by weight, of water.
2. The composition of Claim 1 wherein said water soluble salt of N-phosphonomethylglycine is the sodium, potassium or ammonium salt or a mixture thereof.
3. The composition of Claims 1 or 2 wherein said water present in said dry composition is in the range from about 0.2 to about 2.0 percent by weight of the total composition.
4. The composition of any of Claims 1-3 wherein said liquid surfactant comprises a nonionic surfactant, an anionic surfactant, a cationic surfactant, an amphoteric surfactant or mixtures thereof.
5. The composition of Claim 4 wherein said nonionic surfactant is a polyoxyethylene polyoxypropylene block copolymer, an alkylphenol polyoxyethylene ether, polyoxyethylene oleylether, or mixtures thereof.
6. The composition of Claim 4 wherein said cationic surfactant is an ethoxylated fatty amine surfactant, or surfactant mixtures based thereon.
7. The composition of Claim 4 wherein said amphoteric surfactant is an amine oxide, Aromox C/12, betaines, Lonza-ines, or mixtures thereof.
8. The composition according to any of Claims 1-7, further comprising ammonium sulfate, potassium sulfate, potassium chloride, sodium sulfate, urea, or mixtures thereof.
9. The composition of any of Claims 1-8 which further comprises an ingredient selected from the group consisting of a dispersing agent, a corrosion inhibitor, a thickener, a calcium sequestrant, a defoamer, a synergist, a quick burn additive, a humectant, a dye or pigment, or combinations thereof.

10. The composition according to any of the previous claims in a particular form, preferably granular form, wherein the particles are greater than about 60 mesh.
11. The composition according to any of the previous claims further comprising at least one water-soluble herbicide other than N-phosphonomethylglycine.
12. A process for preparing a dry granular water soluble agriculturally acceptable composition according to any of Claims 1-11, which comprises granulating an admixture of the ingredients, preferably by extrusion and drying said admixture.
13. A process for preparing a composition according to any of Claims 1-11 wherein said ingredients are admixed with water to form admixed composition and thereafter admixed composition is spray dried to form a granular product composition.

Patentansprüche

1. Trockene, wasserlösliche, landwirtschaftlich annehmbare Zusammensetzung, welche N-Phosphonomethylglycin oder ein wasserlösliches Salz von N-Phosphonomethylglycin, zumindest einen Surfactant, der bei Umgebungstemperatur flüssig ist, und der in Wasser geliert, und weniger als etwa 5 Masse-%, vorzugsweise weniger als etwa 2 Masse-%, Wasser umfaßt.
2. Zusammensetzung nach Anspruch 1, worin das wasserlösliche Salz von N-Phosphonomethylglycin das Natrium-, Kalium- oder Ammoniumsalz oder eine Mischung hiervon ist.
3. Zusammensetzung nach Anspruch 1 oder 2, worin das in der trockenen Zusammensetzung vorhandene Wasser im Bereich von etwa 0,2 bis etwa 2,0 Masse-% der Gesamtzusammensetzung vorliegt.
4. Zusammensetzung nach einem der Ansprüche 1 bis 3, worin der flüssige Surfactant einen nicht-ionischen Surfactant, einen anionischen Surfactant, einen kationischen Surfactant, einen amphoteren Surfactant oder Mischungen hiervon umfaßt.
5. Zusammensetzung nach Anspruch 4, worin der nicht-ionische Surfactant ein Polyoxyethylen-Polyoxypropylen-Blockcopolymer, ein Alkylphenolpolyoxyethylenether, Polyoxyethylenoleylether oder Mischungen hiervon ist.
6. Zusammensetzung nach Anspruch 4, worin der kationische Surfactant ein ethoxylierter Fettsäureamin-Surfactant oder darauf basierende Surfactant-Mischungen ist.
7. Zusammensetzung nach Anspruch 4, worin der amphotere Surfactant ein Aminoxyd, Aromox C/12, Betaine, Lon-zaine oder Mischungen hiervon ist.
8. Zusammensetzung nach einem der Ansprüche 1 bis 7, welche ferner Ammoniumsulfat, Kaliumsulfat, Kaliumchlorid, Natriumsulfat, Harnstoff oder Mischungen hiervon umfaßt.
9. Zusammensetzung nach einem der Ansprüche 1 bis 8, welche ferner einen Bestandteil, ausgewählt aus der Gruppe bestehend aus einem Dispergiermittel, einem Korrosionsinhibitor, einem Verdickungsmittel, einem Calcium-Seque-striermittel, einem Entschäumer, einem Synergisten, einem schnellverbrennenden Additiv, einem Anfeuchter, einem Farbstoff oder Pigment oder Kombinationen hiervon, umfaßt.
10. Zusammensetzung nach einem der vorhergehenden Ansprüche in einer bestimmten Form, vorzugsweise granulä-ren Form, worin die Teilchen größer als etwa 60 Mesh sind.
11. Zusammensetzung nach einem der vorhergehenden Ansprüche, welche ferner zumindest ein anderes wasserlös-liches Herbizid als N-Phosphonomethylglycin umfaßt.
12. Verfahren zur Herstellung einer trockenen, granulären, wasserlöslichen, landwirtschaftlich annehmbaren Zusam-mensetzung nach einem der Ansprüche 1 bis 11, welches das Granulieren einer Mischung der Bestandteile, vor-zugsweise durch Extrusion, und Trocknen der Mischung umfaßt.

13. Verfahren zur Herstellung einer Zusammensetzung nach einem der Ansprüche 1 bis 11, bei welchem die Bestandteile mit Wasser gemischt werden, wobei eine gemischte Zusammensetzung gebildet wird, und danach die gemischte Zusammensetzung sprühtrocknet wird, wobei eine granuläre Produktzusammensetzung gebildet wird.

5 Revendications

1. Composition sèche, soluble dans l'eau, acceptable sur le plan agricole, comprenant de la N-phosphonométhylglycine ou un sel soluble dans l'eau de la N-phosphonométhylglycine, au moins un agent tensio-actif qui est liquide à la température ambiante et qui forme un gel dans l'eau, et moins qu'environ 5 % en poids, de préférence moins qu'environ 2 % en poids, d'eau.
2. Composition selon la revendication 1, dans laquelle ledit sel soluble dans l'eau de la N-phosphonométhylglycine est le sel de sodium, de potassium ou d'ammonium ou un mélange de ceux-ci.
3. Composition selon les revendications 1 ou 2, dans laquelle ladite eau présente dans ladite composition sèche est dans la gamme comprise d'environ 0,2 à environ 2,0 % en poids de la composition totale.
4. Composition selon l'une quelconque des revendications 1-3, dans laquelle ledit agent tensio-actif liquide comprend un agent tensio-actif non-ionique, un agent tensio-actif anionique, un agent tensio-actif cationique, un agent tensio-actif amphotère ou des mélanges de ceux-ci.
5. Composition selon la revendication 4, dans laquelle ledit agent tensio-actif non-ionique est un copolymère séquencé de polyoxyéthylène-polyoxypropylène, un éther d'alkylephénole polyoxyéthylène, un oleyléther de polyoxyéthylène, ou des mélanges de ceux-ci.
6. Composition selon la revendication 4, dans laquelle ledit agent tensio-actif cationique est un agent tensio-actif d'une amine grasse éthoxylée, ou des mélanges d'agents tensio-actifs basés sur celui-ci.
7. Composition selon la revendication 4, dans laquelle ledit agent tensio-actif amphotère est un oxyde d'amine, Aromox C/12, des bétaines, Lonzaines, ou des mélanges de ceux-ci.
8. Composition selon l'une quelconque des revendications 1-7, comprenant en outre du sulfate d'ammonium, du sulfate de potassium, du chlorure de potassium, du sulfate de sodium, de l'urée, ou des mélanges de ceux-ci.
9. Composition selon l'une quelconque des revendications 1-8 qui comprend en outre un ingrédient choisi dans le groupe constitué d'un agent dispersant, d'un inhibiteur de corrosion, d'un épaississant, d'un sequestrant de calcium, d'un agent de suppression de la mousse, d'un synergiste, d'un additif provoquant rapidement des effets de brûlure, d'un agent humidifiant, d'une teinture ou d'un pigment, ou des combinaisons de ceux-ci.
10. Composition selon l'une quelconque des revendications précédentes dans une forme particulière, de préférence dans une forme granulaire, dans laquelle les particules ont un diamètre supérieur à environ 0,2 mm (60 mesh).
11. Composition selon l'une quelconque des revendications précédentes, comprenant en outre au moins un herbicide soluble dans l'eau autre que la N-phosphonométhylglycine.
12. Procédé pour préparer une composition sèche, granulaire, soluble dans l'eau, acceptable dans le domaine agricole selon l'une quelconque des revendications 1-11, qui comprend la granulation d'un mélange des ingrédients, de préférence par extrusion et séchage dudit mélange.
13. Procédé pour préparer une composition selon l'une quelconque des revendications 1-11, dans lequel lesdits ingrédients sont mélangés avec de l'eau pour former une composition mélangée et ensuite la composition mélangée est séchée par atomisation afin de former une composition d'un produit granulaire.